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Synthesis and properties of conjugated thiophenes fused onto a dehydro[15]annulene scaffold

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Abstract

A short series of dehydrobenzothieno- and dehydropyridothieno[15]annulene ([15]DBTA and [15]DPTA) hybrids were assembled from thiophene, acetylene, and benzene/pyridine components. The molecules were constructed in a convergent manner and their properties examined optically, electrochemically, and thermally. In addition to lowered energy of electronic transitions of the 15-membered macrocycles, their emissive properties are discussed. The observed trends correspond with previously reported [14]annulenes, and are further rationalized using DFT (B3LYP/6-311G**) calculations. ***To cite this article: M. J. O'Connor et al., C. R. Chimie 12 2009.***

Keywords: Annulene; Thiophene; Acetylene; Macrocycle; DFT calculations

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1. Introduction

Highly unsaturated conjugated compounds have attracted substantial interest from synthetic, theoretical, and materials chemists in recent years [1]. Specifically, highly delocalized alkyne-containing systems [2] have elicited most of this attention for several reasons. First, the development of new synthetic procedures based on organometallic cross-coupling reactions [3] has provided access to a wide variety of compounds whose preparation was not previously possible. Second, many of these carbon-rich systems and macrocycles exhibit important materials properties such as nonlinear optical (NLO) activity [4], liquid crystalline behavior [5], and molecular switching [6]. Recent developments have shown that dehydrobenzoannulenes [7] and other related phenyl−acetylene macrocycles [8] are useful precursors to a number of carbon-rich polymeric systems, such as molecular tubes [9], ladder polymers [10], and novel allotropes of carbon [11]. Thus, it is essential to have easy access to these high carbon content molecules in sufficient quantities via straightforward synthetic methods if their technological potential is to be explored and eventually utilized.

We have been studying acetylene-rich dehydrobenzoannulenes (DBAs) [7,12] with the goal of examining their diverse chemical and physical properties. Our group has largely focused on the development of new or improved synthetic techniques for the assembly of such macrocycles. Our current

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methodologies allow us to introduce donor and/or acceptor functionalities on the phenyl rings of the DBA in a judicious manner, thus effectively "tuning" the optoelectronic properties of the annulene [12a]. To explore further DBA functionalization for detailed structure–property relationship studies, we chose to incorporate thiophene moieties onto the dehydroannulene skeleton [13]. The choice of thiophene as the fused aromatic ring was inspired by this moiety's materials applicability such as the chemical/electrochemical polymerizability of thiophene, the ability to form two-dimensional π-systems useful for electronics and photonics, the easier polarizability of thiophene, and the interaction among the individual macrocycles due to the lone pairs on the sulfur in each thiophene ring [14]. With respect to other heteroaromatics, thiophenes in general are easier to manipulate and to functionalize over pyrroles or furans, allowing easy access to tailored thiophene derivatives. Furthermore, by locking the conjugated system into planarity, thiophene-containing macrocycles [14d,e,15] and cyclic thiophene–acetylene hybrids [16–19] have the potential to more efficient materials because of geometrically enforced π-orbital overlap with increased quinoidal character of the delocalized system and thus a decreased optical band gap [20].

Prior studies on thieno-fused dehydroannulenes such as **1** [17] and **2** [18] (Fig. 1) relied on metal-mediated intermolecular couplings for macrocycle construction. The structures of the starting materials, however, limited the resultant molecules to either C_{nh}- or D_{nh}-symmetry. In 2000 we reported the preparation of dehydrothieno [18]annulenes ([18]DTAs, e.g., **3**) having lower symmetries (C_{2v}, C_s) [13a,b]. While these macrocycles could be assembled in a systematic, stepwise manner, poor stability of the thienyldiyne intermediates necessitated exploration of other topologies. More recently, we described the synthesis and optoelectronic properties of a series of thiophene-containing [14]DBA/DTA hybrids (e.g., **4**, henceforth [14]DBTAs) and the corresponding all-thiophene containing [14]DTAs (e.g., **5**) [13c]. That study showed that subtle changes in molecule symmetry can "tune" the properties of annulenes. For example, the UV–vis spectra of this class of macrocycles showed that the large transitions remain essentially the same, but displayed distinct differences in the low-energy vibronic region. Expanding on our success with [15]DBAs [12a,c,e] and our further understanding of thieno-fused annulenes, this report details the synthesis and characterization (thermal, optical, electro-chemical, computational) of [15]DBTA hybrids **6–9** (Fig. 2) and [15]DPTA (dehydropyridothieno annulene) hybrids **10** [12c] and **11**.

2. Results and discussion

2.1. Macrocycle synthesis

All six macrocycles were constructed in a convergent fashion from the synthons given in Fig. 3. Dihaloarenes **12–14** are commercially available, whereas diynes **15–17** were prepared starting from the appropriate dihalothiophenes using our previously reported syntheses [12c,13c].

An example of symmetrical macrocycle synthesis is given in Scheme 1. Selective removal of the TMS group in diyne **16** with K_2CO_3 in MeOH/THF followed by cross-coupling to 1,3-diiodobenzene (**12**) afforded precursor **18** (**pre-6**) in 86% yield. Desilylation with TBAF and cyclization using modified Glaser–Eglinton conditions generated hybrid **6** in 55% yield.

Preparation of the only unsymmetrical macrocycle, **7**, is shown in Scheme 2. Selective desilylation of diyne **15** as described above and then cross-coupling to 1-bromo-3-iodobenzene (**13**) yielded **19**, which proved to be moderately sensitive to silica. After rapid

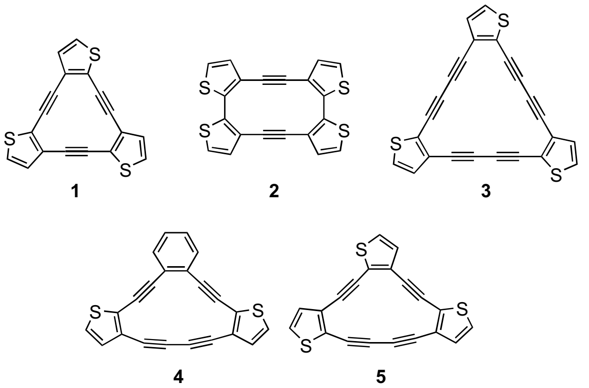

Fig. 1. Examples of known thieno-fused dehydroannulenes.

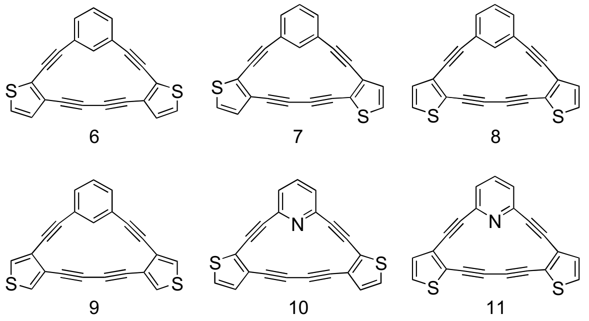

Fig. 2. Target thieno-fused dehydro[15]annulenes **6–11**.